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(54) **Glass substrate and leveling thereof**

(57) A glass substrate having a surface which has been leveled, preferably to a flatness of 0.04-1.3 nm/cm<sup>2</sup> of the surface, by local plasma etching is provided. A glass substrate whose surface carries microscopic peaks and valleys is leveled by measuring the height of

peaks and valleys on the substrate surface, and plasma etching the substrate surface while controlling the amount of plasma etching in accordance with the height of peaks.

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**Description**

[0001] This invention relates to glass substrates which are useful as silica glass substrates for reticles used in the most advanced application among semiconductor-related electronic materials, and silica glass substrates or silica glass chips which are expected to find wide-spreading use in the fields of microelectronics, micro-optics and micro-analyses; and a method for leveling the surface thereof.

**BACKGROUND**

[0002] Quality parameters of photomask-forming silica glass substrates include the size of defects, the density of defects, flatness, surface roughness, the opto-chemical stability of material, and the chemical stability of surface. Of these parameters, the quality relating to the flatness on substrates is more strictly required to comply with the trend of ICs toward finer-circuitry. It is highly probable that the design rule of interconnection to be transferred to silicon wafers will fall below 100 nm. Then, silica glass substrates for photomasks must have a flatness below 0.3  $\mu\text{m}$  for the 6025 substrate (152 mm by 152 mm by 6.35 mm). Specifically, when a wiring pattern on a photomask is optically transferred to a silicon wafer, the exposure surface is desired to be as flat as possible. The flatness of the exposure surface is correlated to many factors including the material and thickness of a light-shielding film, the type of wiring pattern and the location within the exposure system although the flatness of glass substrate is one of predominant factors. If the design rule of interconnection is reduced to below 100 nm in the future and the 6025 substrate yet has a flatness in excess of 0.3  $\mu\text{m}$ , then the critical dimension (CD) accuracy of the wiring pattern transferred to the silicon wafer exceeds the permissible range. This leads to a failure to establish fine-circuitry devices.

[0003] The current technology of leveling or flattening silica glass substrates for photomasks is an extension of the traditional polishing technology. The surface flatness achievable with the current technology is on the average about 0.5  $\mu\text{m}$  at best for the 6025 substrate. Substrates having a flatness of less than 0.5  $\mu\text{m}$  can be obtained, but in very low yields. This is because in the traditional polishing technology, it is possible to roughly control the polishing rate over the entire surface of a substrate, but it is impossible in a practical sense to specify a leveling recipe for each of starting substrates in accordance with their shape and individually polish the substrates for evening out irregularities. Also, when double-sided lapping on a batchwise basis is used, for example, it is very difficult to control variations within each batch and between batches. When single-side lapping on a single-wafer basis is used, a difficulty arises in that variations occur in conformity to the shape of starting substrates. In either case, it is difficult to consistently manufacture substrates with improved surface flatness.

[0004] An object of the invention is to provide a glass substrate having good or improved surface flatness and a glass substrate leveling method ensuring that a glass substrate having improved surface flatness is easily obtainable. Indeed, using this method a glass substrate having a fully flat surface may be obtained.

[0005] It has been found that when a starting glass substrate having a surface carrying microscopic peaks and valleys is plasma etched locally at the peaks while controlling the amount of plasma etching in accordance with the heights of peaks, there is obtained a glass substrate having an improved flatness, preferably a flatness of 0.04 nm to 1.3 nm per square centimeter of the surface. In the case of the 6025 substrate (152 mm by 152 mm by 6.35 mm) which is the mainstream among photomask substrates, for example, substrates having a flatness of 0.01  $\mu\text{m}$  to 0.3  $\mu\text{m}$  can be provided.

[0006] The technique of processing material surfaces by plasma etching is found, for example, in JP-A 5-160074. However, this technique is applicable to only silicon wafers. Its object is to eliminate variations in thickness of material, different from the present invention's object of leveling out the surface of glass substrates. JP-A 10-273788 discloses a technique of processing quartz glass using a plasma. This relates to the means for producing complex surfaces such as aspheric lenses and differs in object and field from the technique of leveling out the surface of glass substrates such as photomask substrates.

[0007] In one aspect, the invention provides a glass substrate having a surface which has been leveled by local plasma etching.

[0008] Preferably, the surface of the glass substrate has a flatness of 0.04 to 1.3 nm per square centimeter of the surface. The glass substrate may often be a silica glass substrate. Preferably, the substrate will have dimensions of  $152 \pm 0.2$  mm by  $152 \pm 0.2$  mm by  $6.35 \pm 0.1$  mm.

[0009] In another aspect, the invention provides a method for leveling a surface of a glass substrate, the surface carrying microscopic peaks and valleys, the method comprising the steps of measuring the heights of peaks and valleys on the substrate surface, and plasma etching the substrate surface while controlling the amount of plasma etching in accordance with the heights of peaks.

FURTHER EXPLANATION; OPTIONS AND PREFERENCES

**[0010]** The invention employs a plasma etching technique as the means for producing high-flatness glass substrates. The starting glass substrate has a surface carrying microscopic irregularities, that is, peaks and valleys. The first step is to measure the heights of peaks and valleys on the substrate surface. In the second step, plasma etching is carried out on the substrate surface while controlling the amount of plasma etching in accordance with the heights of peaks, specifically locally changing the amount of plasma etching (i.e., amount of substrate glass etched away) so that a more amount of substrate glass may be etched away in an area of a high peak height and a less amount of substrate glass be etched away in an area of a low peak height.

**[0011]** Specifically, a plasma generating housing is positioned above a peak site on the glass substrate surface where plasma etching is carried out. Neutral radical species generated in the plasma isotropically attack the glass substrate surface at that site whereby the site and the close area around it are etched away. In areas of the glass substrate surface outside the plasma generating housing, no plasma is generated and little or no etching takes place, though some etchant gas strikes against the surface. When the plasma generating housing is moved above the starting glass substrate, the rate of movement of the housing is controlled in accordance with the heights of peaks on the starting glass substrate so that a glass substrate having excellent flatness is eventually obtainable.

**[0012]** It is necessary that the surface shape or topography of the starting glass substrate be previously determined, that is, the heights of peaks and valleys on the glass substrate surface be previously measured. Surface shape measurement may be done by any methods. It is desired in view of the target flatness that such measurement be of high precision, and thus, an optical interference method is a typical measurement. In accordance with the surface shape or the heights of peaks, the rate of movement of the plasma generating housing is computed. Then the rate of movement is controlled to be slow in an area of a high peak height so as to provide a more etching amount.

**[0013]** The plasma generating housing may be of any structure. In one exemplary system, the glass substrate is sandwiched between a pair of electrodes, a plasma is created between the substrate and the electrode by application of a radio frequency power, and an etchant gas is flowed therethrough to generate radical species. In another system, an etchant gas is passed through a waveguide where a plasma is created by microwave oscillation, and the flow of radical species thus generated is impinged against the substrate surface. The etchant gas is selected depending on the identity of glass substrate. For silica glass substrates for photomasks, a halide gas or a gas mixture containing a halide gas is preferred. The halide gas is exemplified by methane tetrafluoride, methane trifluoride, ethane hexafluoride, propane octafluoride, butane decafluoride, hydrogen fluoride, sulfur hexafluoride, nitrogen trifluoride, carbon tetrachloride, silicon tetrafluoride, methane trifluoride chloride or boron trichloride.

**[0014]** To control the rate of movement of the plasma generating housing in accordance with the heights of peaks on the surface of the starting glass substrate as mentioned above, a computer may be used. Since the movement of the plasma generating housing is relative to the substrate, the substrate itself may be moved instead.

**[0015]** The glass substrate thus processed reaches a very high degree of flatness. The desired flatness is, though not limited to, 0.04 nm to 1.3 nm, especially 0.04 nm to 0.86 nm per square centimeter of the substrate surface. The glass substrate is preferably dimensioned  $152 \pm 0.2$  mm by  $152 \pm 0.2$  mm by  $6.35 \pm 0.1$  mm (named 6025 substrate). In the case of 6025 substrates which are most often used as the photomask-forming glass substrate, a high flatness glass substrate having a flatness of 0.01  $\mu$ m to 0.3  $\mu$ m can be obtained.

**[0016]** Under certain plasma etching conditions, the surface of the glass substrate thus obtained can have surface roughness or a work-degraded layer. In such a case, if necessary, the plasma etching may be followed by a very short time of polishing which does bring substantially little change of flatness.

**[0017]** Preferred for the measurement of flatness/unevenness considering measurement precision is an optical interference method in which coherent light (matched phase relationship) as typified by laser light is directed to the substrate surface and reflected thereby, and a difference in height of substrate surface points is observed as a phase shift of reflected light.

**[0018]** Thus one can provide a glass substrate having a high flatness, specifically a flatness of 0.04 nm to 1.3 nm/cm<sup>2</sup> of the substrate surface, which is suited for use as silica glass substrates for photomasks used in the photolithography of great interest in the fabrication of ICs, and silica glass substrates and silica glass chips which are expected to find wide-spreading use in the fields of microelectronics and microanalyses. The invention thus contributes to the achievement of finer patterns in the semiconductor field and a further advance of the micro-system field.

EXAMPLE

**[0019]** Examples of the invention are given below by way of illustration and not by way of limitation.

Example 1

[0020] The starting substrate used was a quartz substrate having a pair of square surfaces of 152 mm by 152 mm and a thickness of 6.35 mm.

[0021] One surface of the quartz substrate was measured by an optical interference flatness meter, finding a flatness of 3.7 nm/cm<sup>2</sup> of the surface. Based on the thus obtained data about microscopic peaks and valleys on the substrate surface, the rate of movement of a plasma generating housing which was located above the substrate was computed. Plasma etching was carried out on the substrate surface by moving the plasma generating housing along the substrate surface at the controlled rate. The plasma generating housing of high-frequency type (150 W) had cylindrical electrodes of 75 mm diameter. The etchant gas used was methane tetrafluoride. After plasma etching was carried out over the entire substrate surface, that surface of the quartz substrate was measured again by the optical interference flatness meter, finding a flatness of 0.21 nm/cm<sup>2</sup> of the surface.

Examples 2-9

[0022] As in Example 1, quartz substrates having surfaces with different flatness values were plasma etched, obtaining quartz substrate having surfaces leveled. The flatness values per square centimeter of the surface before and after plasma etching are shown in Table 1.

Table 1

	Example							
	2	3	4	5	6	7	8	9
Initial flatness (nm)	5.2	4.0	2.3	3.2	3.3	4.1	2.9	1.5
Flatness after plasma etching (nm)	0.74	0.48	0.17	0.39	0.52	0.82	0.39	0.04

[0023] The invention ensures that quartz substrates having a surface leveled to a flatness of 0.04-1.3 nm/cm<sup>2</sup> of the surface are readily produced.

[0024] The disclosure of Japanese Patent Application No. 2001-122369 (the present priority application) is incorporated herein by reference.

[0025] Reasonable modifications and variations are possible from the specifically described examples in the light of the general teachings herein.

Claims

1. A glass substrate having a surface which has been levelled by local plasma etching.
2. The glass substrate of claim 1 wherein the surface of the glass substrate has a flatness of less than 0.3  $\mu\text{m}$  per square centimetre of the surface.
3. The glass substrate of claim 1 wherein the surface of the glass substrate has a flatness of 0.04 nm to 1.3 nm per square centimetre of the surface.
4. The glass substrate of claim 1 which is a silica glass substrate.
5. The glass substrate of claim 1 which has dimensions of  $152 \pm 0.2$  mm by  $152 \pm 0.2$  mm by  $6.35 \pm 0.1$  mm.
6. The glass substrate of claim 5 wherein a surface of the glass substrate has a flatness of 0.01  $\mu\text{m}$  to 0.3  $\mu\text{m}$  per square centimetre of the surface.
7. A method for levelling a surface of a glass substrate, the surface carrying microscopic peaks and valleys, the method comprising the steps of:

measuring the heights of peaks and valleys on the substrate surface, and  
plasma etching the substrate surface while controlling the amount of plasma etching in accordance with the heights of peaks.

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**8.** The method of claim 7 wherein the measuring step is performed using an optical interference method.

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## EUROPEAN SEARCH REPORT

Application Number  
EP 02 25 2766

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 01, 29 January 1999 (1999-01-29) & JP 10 273788 A (MORI YUZO; NIKON CORP), 13 October 1998 (1998-10-13) * abstract *	1,7	C03C23/00 H01L21/31 C03B19/00 C23F1/00
Y	-----	1-8	
X	EP 0 514 046 A (HUGHES AIRCRAFT CO) 19 November 1992 (1992-11-19) * column 3, line 25-33 *	1,7	
Y	* column 5, line 14 - column 6, line 26; claims 1-10 *	1-8	
X	US 4 515 652 A (GIMPELSON GEORGE E ET AL) 7 May 1985 (1985-05-07) * column 2, line 11 - column 3, line 30; claims 1-19 *	1,7	
Y	-----	1-8	
A	EP 0 317 794 A (IBM) 31 May 1989 (1989-05-31) * page 2, line 12-38; claims 1-9 *	1-8	TECHNICAL FIELDS SEARCHED (Int.Cl.7)  C03C H01L C03B C23F
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 2 August 2002	Examiner Maurer, R
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 25 2766

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
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02-08-2002

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
JP 10273788	A	13-10-1998	NONE		
EP 0514046	A	19-11-1992	US	5254830 A	19-10-1993
			DE	69228020 D1	11-02-1999
			DE	69228020 T2	27-05-1999
			EP	0514046 A1	19-11-1992
			IL	101474 A	27-11-1995
			JP	2565617 B2	18-12-1996
			JP	5160074 A	25-06-1993
		KR	9610336 B1	30-07-1996	
US 4515652	A	07-05-1985	EP	0155668 A2	25-09-1985
			JP	61001029 A	07-01-1986
EP 0317794	A	31-05-1989	US	4836887 A	06-06-1989
			DE	3852619 D1	09-02-1995
			DE	3852619 T2	06-07-1995
			EP	0317794 A2	31-05-1989
			JP	1161838 A	26-06-1989
			JP	1950128 C	10-07-1995
			JP	6082638 B	19-10-1994

EPO FORM P409

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82